

Latest Enhancements to the GC/MS Analysis of Gasoline by ASTM Method D-5769

Application Note

Agilent Technologies 6890/5973 GC/MSD System

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Abstract

The 6890/5973 GC/MSD system and its latest ChemStation software each contain enhancements that refine the analysis of aromatics in gasoline by ASTM Method D-5769. The improvements in the MSD hardware are the addition of a high energy dynode electron multiplier and increased scanning speed. The improvements in the software are easy entry of weights, easy signal to noise calculation, weight and volume percent calculated in the customized report, use of API index number, and expanded Help files. The improvements in the GC/MS method are fast temperature programming, carrier gas programming, high split ratio, narrow mass range, and electron multiplier programming. The performance of the 6890/5973 GC/MSD system with respect to ASTM Method D-5769 has been characterized. It was found that excellent toluene linearity, fast 20 minute analysis times, and excellent precision on duplicates could be achieved.

Keywords

Benzene, toluene, aromatics, gasoline, reformulated gasoline, RFG, gas chromatography/mass spectrometry, GC/MS, ASTM D-5769

Introduction

ASTM Method D-5769 is for analysts who have to certify the aromatic content in finished motor gasoline. These analysts are gasoline producers, manufacturers, blenders, distributors, independent testing laboratories, and regulatory bodies. A recent review by Vince Giarrocco of Agilent Technologies details the background of the

reformulated gasoline analytical methodology.¹ An earlier Agilent Technologies Applications Brief describes the use of the 5972 MSD as applied to the first version of this ASTM method.²

The latest enhancements afforded by using the 6890/5973 GC/MSD here provide an improved means to validate compliance with government regulations and enhance productivity, and are more specific to the latest version of D-5769. The hardware and software recommendations are listed in Table 1.

Table 1. Hardware and software recommendations

GC:	6890
GC Consumables:	60 m × 0.25 mm ID, 1.0µm HP-1 P/N 19091Z-236 Split/Splitless liner with glass wool P/N 19251-60540 Merlin Microseal P/N 5181-8833
ALS:	7673 with nanoliter adapter
MS:	5973A Mass Selective Detector
MSD ChemStation:	Aromatics in Gasoline mode MSD Productivity ChemStation Software

Software Enhancements

The improvements in the software are easy entry of sample weights, internal standard weights, density, easy signal to noise calculation, inclusion of uncalibrated compounds in the calculations, weight and volume percent calculated in the customized report, use of API index number, and expanded Help files that are specific to this analysis.

When recalibration utilizes a new batch of calibration standards, the individual amounts defining the calibration curve will need to be updated. This process is automated if the calibration standards are purchased from a vendor that also supplies an update disk. The individual amounts will be inserted for each compound that has a name and a CAS number that matches the one in the file.

The gasoline analysis method ASTM D5769 calls for a signal to noise check on the extracted ion chromatogram from the GC/MS analysis of a 0.01 weight % solution of 1,4-diethylbenzene. With a few simple click and drag operations the check is made and a special report is printed out.

The calibrated components do not account for all the aromatics in gasoline. These components are identified by the existence of peaks with characteristic ions in specified retention time ranges. The quantitation of the uncalibrated components utilizes the calibration curve of an appropriate calibrated component.

The ASTM method also calls for a report of the weight % and volume % for each aromatic compound in the sample. These are provided by the software via a standard internal standard report that is enhanced with sample weight, sample density, ISTD weight, weight %, and volume %. Calculation of these quantities requires sample specific information. The sample weight and sample density need to be input by the operator.

There are also several editing features that are enhancements beyond the standard quantitation software, such as use of sample density or API index number and the y-intercept test for each calibration curve.

GC/MS Enhancements

There are two approaches to GC analysis of gasoline. One requires long analysis times, high resolution columns, and universal detectors. The other uses mass selective detectors and can result in shorter analysis times with less stringent chromatographic resolution requirements. Detailed hydrocarbon analysis (DHA) is an example of the former approach while D-5769 and its enhancements described here is an example of the later. This ASTM method has only a few mandated conditions. The refinement of the final method is at the individual laboratory discretion. The major requirements are that a methylsilicone column is used and the mass spectrometer is operated in full scan mode generating electron impact ions at 70 electron volts. There are also requirements of

minimum column resolution, sensitivity, and data collection rate; these will be discussed later.

Experimental

In this work several chromatographic method enhancements were employed to enhance throughput. In the past for Method D-5769 run times of 30 to 50 minutes have been common in some laboratories. In order to attain a more desirable 20 minute run time, a starting oven temperature of 120° was used with a relatively fast two-level temperature program.³ Holding the helium carrier gas flow at a constant 35 cm/sec during the run was also employed. This is 40% above the flow used for maximum efficiency, i.e., maximum chromatographic resolution. The details are shown in Table 2.

Even with 0.1 microliter injected and split the suggested 250 to 1, column overloading and toluene nonlinearity were observed. By raising the split ratio to 1100 to 1, the GC peaks shapes improved markedly. But at 15% toluene levels a nonlinear curve was still observed. Method D-5769 calls for the use of m/z 91 for toluene quantitation. This is the base peak. However, use of the carbon 13 isotope peak of m/z 92, which is 54% of m/z 91 produces a linear calibration curve.⁴ Use of m/z 65, which is 10% of m/z 91 also, gives a linear calibration curve. Of the three possible mass peaks, the use of m/z 92 gives the best signal to noise along with a linear calibration curve. The high use of helium for the 1100 to 1 split ratio is

Table 2. Recommended Instrumental Parameters

GC Injection Port:	250°C Split 1100:1
GC Oven Ramp:	120°C for 0.5 minutes 3°C/minute to 140°C 10°C/minute to 250°C 0 minutes hold at 250°C
Carrier Gas:	Helium
GC Pressure Program:	0.3 mL/minute for 1.0 minutes 1.0 mL/min at 1.0 minutes 35 cm/second constant flow Vacuum compensation ON Gas saver ON after 1 minute
ALS:	5µL syringe Nanoliter adapter, stop = 1 (0.1µL injection size)
MSD:	Transfer Line: 280°C Ion Source: 200°C Quadrupole: 150°C Solvent Delay: 3 minutes Electron Energy: 70 eV Emission current: 35 µamps Mass Range: 60 to 170 Daltons Scan Speed: 2 ³ A/D samples Autotune: Standard Multiplier Voltage: Autotune value (1153 volts) +200 volts after 6.0 minutes

somewhat wasteful and so the "gas saver" mode is used to reduce the split flow at times other than injection.

The 5973 uses a high energy dynode electron multiplier that incorporates enhanced ion optics to reduce noise and increase sensitivity. Special ion focusing elements concentrate the ion beam exiting the quadrupole on the 10 kV high energy dynode where a conversion to electrons takes place. This gives higher sensitivity and longer multiplier life.

The high energy dynode is 90° off-axis to minimize noise. Further detector noise reduction is accomplished by careful shielding of the electron multiplier and high energy dynode. This type of detector has increasing sensitivity with mass, which improves the detection of the heavier gasoline components.

The electron multiplier voltage obtained with Autotune is used for benzene and toluene. It is then raised programmatically 200 volts

higher for the remaining components. This assures that the very highest toluene levels that are in some gasoline blending stocks will not overload the detector electronics and that there is sufficient signal for the low level components containing ten carbons and above.

Method D-5769 requires at least five mass spectral scans to be taken over the top half of the GC peak. According to Mathews and Hayes⁵ if the worst case error is to be kept below 1%, at least nine scans must be taken. There is a real quantitation benefit to having as many scans as possible over the GC peak. However, the signal to noise ratio is adversely affected. Therefore, a compromise is needed. The 5973 scans twice as fast as its predecessor, the 5972. In real terms this means that with an A/D setting of 2³ selected, 6.5 scans per second are taken. For the 1,4-diethylbenzene peak this represents 27 scans, reducing the sampling error to 0.1%, which is quite acceptable. These conditions yield a signal to noise ratio of 71 to 1 for the 0.01 wt % sample of 1,4-diethylbenzene.

Additionally, the mass range to use was explored. While Method D-5769 suggests that a mass range of 50 to 350 could be used, it is important to note that the highest mass required in the quantitation is m/z 148. Some of the higher uncalibrated compounds that may need to be quantitated separately have ions no higher than m/z 168.⁶ Therefore, a narrow mass range of m/z 60 to 170 was used to maximize the number of scans.

Results

Figure 1 is the total ion chromatogram of a gasoline test sample, RFA003 QC. Note all compounds elute between 3 and 20 minutes. Figure 2 is a typical report for an RFA sample using the Aromatics in Gasoline software. Figure 3

shows the final linear calibration curve for toluene utilizing the high split ratio, electron multiplier voltage programming, and change of quant ion. The analysis of gasoline by Method D-5769 is not simple and requires careful attention to operational parameters as well as

sample preparation and further method refinements.⁴ It was found that excellent toluene linearity, fast 20 minute analysis times, and excellent precision on duplicates could be achieved with the 6890/5973 GC/MSD.

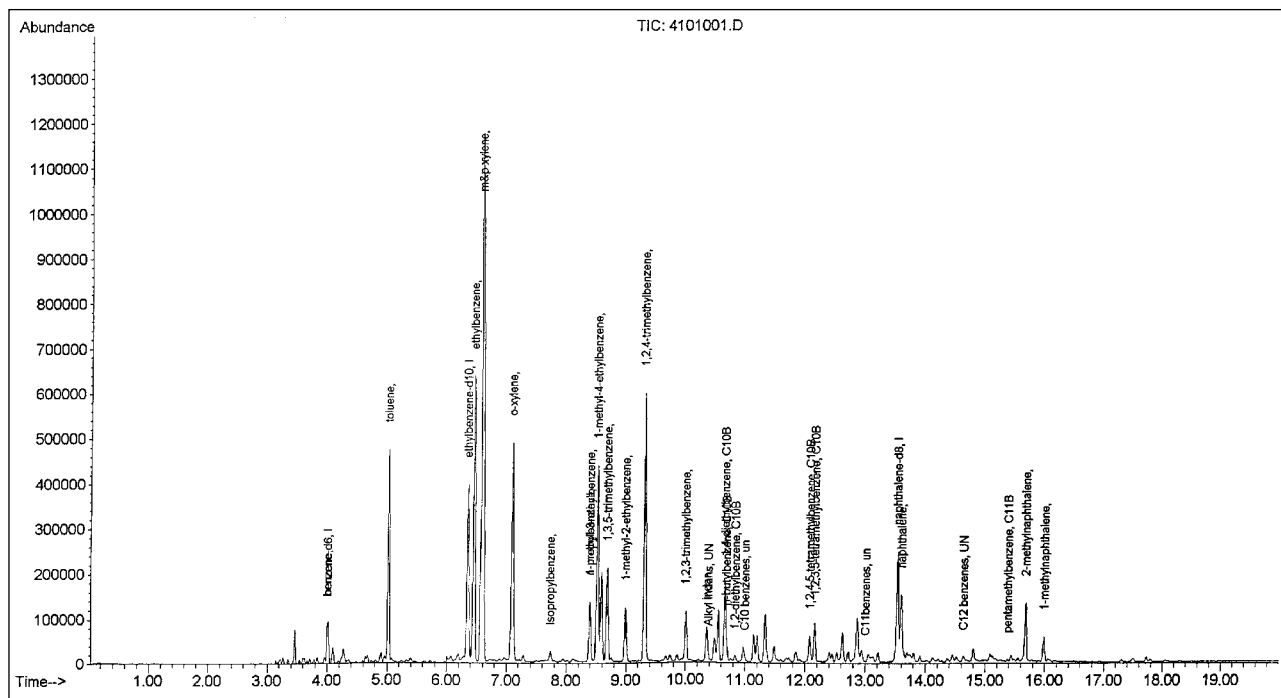


Figure 1. Total ion chromatogram of a gasoline test sample, RFA003 QC.

Aromatics Quantitation Report				(Not Reviewed)		
Data File : C:\HPCHEM\2\DATA\92\1801006.D				Vial: 18		
Acq On : 2 Sep 96 17:27				Operator: R Leibrand		
Sample : rfa3				Inst : 5973		
Misc : 5973				Multiplr: 1.00		
MS Integration Params: RTEINT.P						
Quant Time: Sep 2 18:53 1996				Quant Results File: RFG6890B.RES		
SampWt: 1.2818		SampDens: 0.7501		IstdWt: 0.0569		
Quant Method : C:\HPCHEM\2\METHODS\RFG6890B.M (RTE Integrator)						
Title : Gasoline Aromatics System						
Last Update : Mon Sep 02 18:45:01 1996						
Response via : Initial Calibration						
DataAcq Meth : RFG6890B						
Internal Standards		R.T.	QIon	Response	Conc	Units Dev(Min)

1) benzene-d6		3.94	84	143289	22.76	mg 0.02
3) ethylbenzene-d10		6.32	116	191828	22.76	mg 0.03
17) naphthalene-d8		13.52	136	519787	11.38	mg 0.02
System Monitoring Compounds						
Aromatic Compounds				Wt%	Vol%	
2) benzene		3.96	78	106819	1.33	1.13
4) toluene		4.98	92	492998	9.21	7.92
5) ethylbenzene		6.43	106	321130	2.45	2.10
6) m&p xylene		6.57	106	978127	6.13	5.29
7) o-xylene		7.08	106	335231	2.17	1.84
8) Isopropylbenzene		7.72	120	9665	0.08	0.07
9) n-propylbenzene		8.37	120	64838	0.52	0.45 #
10) 1-methyl-3-ethylbenzene		8.37	120	64838	0.52	0.45 #
11) 1-methyl-4-ethylbenzene		8.51	120	237310	1.67	1.45
12) 1,3,5-trimethylbenzene		8.67	120	157941	0.84	0.73
13) 1-methyl-2-ethylbenzene		8.97	120	67186	0.49	0.42
14) 1,2,4-trimethylbenzene		9.30	120	434304	2.49	2.12
15) 1,2,3-trimethylbenzene		10.00	120	79801	0.47	0.40
16) indan		10.35	117	110913	0.30	0.23
18) 1,4-diethylbenzene		10.65	119	197255	0.73	0.63 #
19) n-butylbenzene		10.68	91	36861	0.09	0.07 #
20) 1,2-diethylbenzene		10.82	105	6707	0.03	0.03
21) 1,2,4,5-tetramethylbenzene		12.07	134	43624	0.21	0.18
22) 1,2,3,5-tetramethylbenzene		12.15	134	59607	0.30	0.25
23) naphthalene		13.59	128	285796	0.47	0.40
24) pentamethylbenzene		15.36	148	3758	0.02	0.02
25) 2-methylnaphthalene		15.66	142	176980	0.42	0.35
26) 1-methylnaphthalene		15.97	142	71005	0.18	0.15
27) C10 benzenes		11.00	134	238008	1.21	1.01
28) C11benzenes		13.00	148	117323	0.56	0.46
29) C12 benzenes		14.64	162	27702	0.13	0.11
30) Alkyl Indans		10.39	117	299343	0.78	0.60
Total:				33.80	28.86	

(#) = qualifier out of range (m) = manual integration						
1801006.D RFG6890B.M		Mon Sep 02 18:53:55 1996			Page 1	

Figure 2. RFA sample using the Aromatics in Gasoline software.

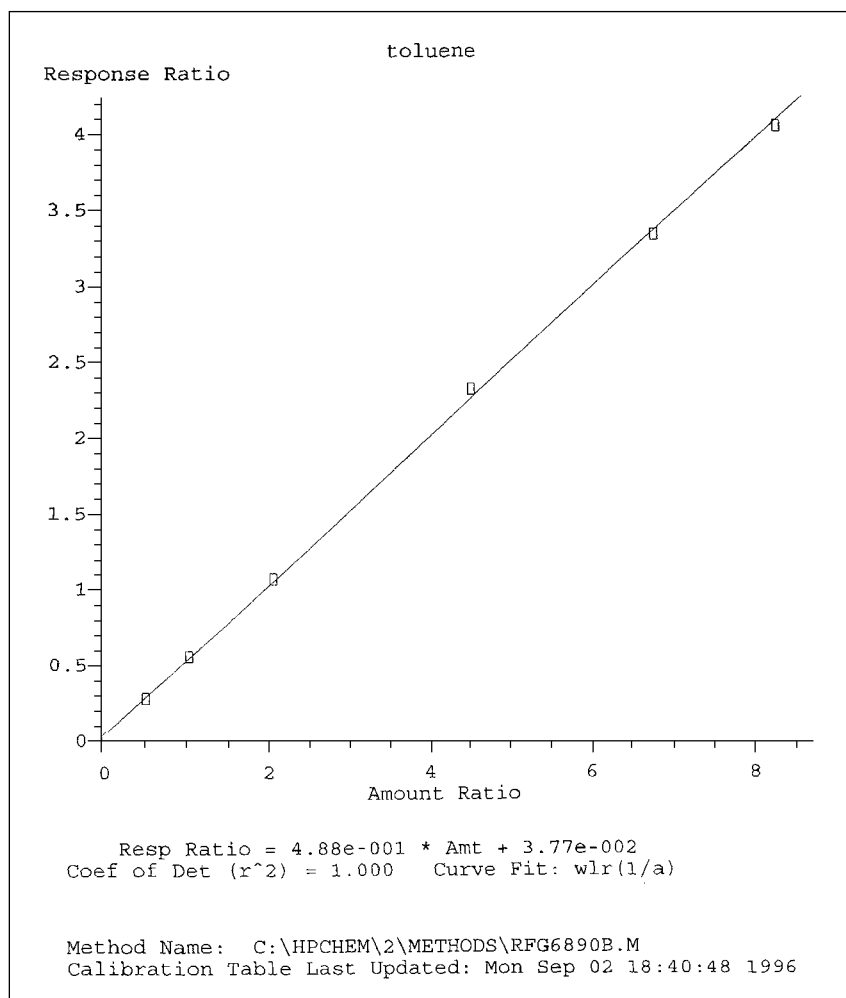


Figure 3. Final linear calibration curve for toluene utilizing the high split ratio, electron multiplier voltage programming and change of quant ion.

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